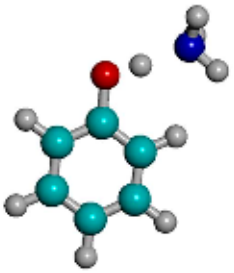
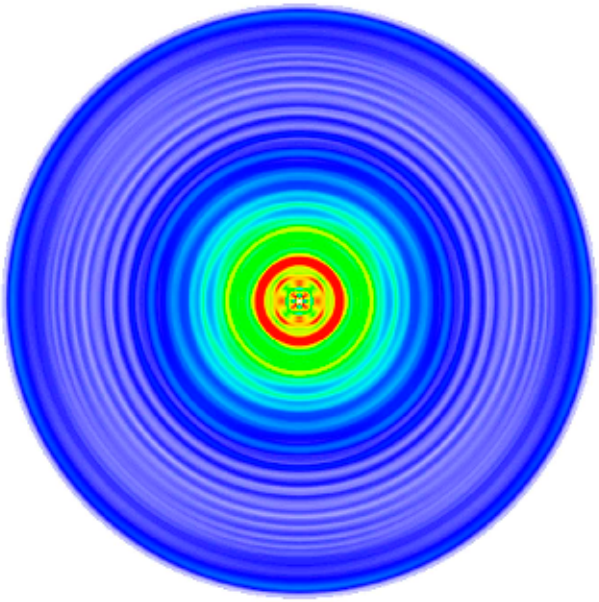


V Jornadas de Jóvenes Investigadores en Física Atómica y Molecular



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Full-dimensional ab initio potential energy surface and dynamics for the H_7^+ cluster

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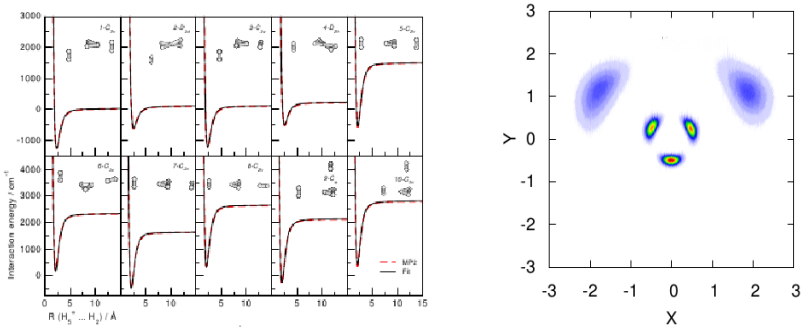
Full-dimensional ab initio potential energy surface is constructed for the H_7^+ cluster [1]. The surface is a fit to roughly 160000 interaction energies obtained with second-order Möller–Plesset perturbation theory (MP2) and the cc-pVQZ basis set, using the invariant polynomial method [2]. We employ permutationally invariant basis functions in Morse-type variables for all the internuclear distances to incorporate permutational symmetry with respect to interchange of H atoms into the representation of the surface. We describe how different configurations are selected in order to create the database of the interaction energies for the linear least squares fitting procedure. The root-mean-square error of the fit is 170 cm^{-1} for the entire data set. The surface dissociates correctly to the H_5^++H_2 fragments. A detailed analysis of its topology (see Figure 1), as well as comparison with additional ab initio calculations, including harmonic frequencies, verify the qua- lity and accuracy of the parameterized potential. This is the first attempt to present an analytical +representation of the 15-dimensional surface of the H_7^+ cluster for carrying out dynamics studies [3]. Diffusion Monte-Carlo and Path Integral Monte-Carlo simulations are carried out for both H_7^+ and D_7^+ to obtain their ground vibrational states and thermal equilibrium states, respectively. Quan- tum vibrational zero point energy (ZPE) and dissociation energies for the reactions $H_7^+ \rightarrow H_5^+ + H_2$ and $D_7^+ \rightarrow D_5^+ + D_2$ are computed.



Left panel: 5 2Interaction energies for the $H_5^+ \ldots H_2$ as a function of the intermolecular distance R connecting the centers of masses of the H_3^+ core (within the H_5^+), and the other H_2. Right Panel: Projection of the probability density of H_7^+ on the H_7^+ plane at T=10K as a function of the cartesian coordinates X e Y (in Angstroms).

[1] P. Barragán, R. Prosmiti, Y. Wang, and J.M. Bowman, J. Chem. Phys. 136, 224302 (2012).

[2] B.J. Braams and J.M. Bowman, Inter. Rev. Phys. Chem. 28, 577 (2009).

[3] P. Barragán, R. Pérez de Tudela, R. Prosmiti, C. Qu, and J.M. Bowman, J. Chem. Phys. In preparation (2013).